SYNOPSIS

Synthesis of 2D Metal Oxide Nanostructures: Optical and Optoelectronic Properties for Photodetector Device Application

Submitting to

Research & Recognition committee (RRC)

Subject: Physics

under

Faculty of Science and Technology

by

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November 2020

Title:

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1. Introduction:

Photodetectors (PDs) with high sensitivity are highly desirable in many applications, such as environmental monitoring, biological / chemical analysis, astronomical studies, and missile detection [1-3]. PDs with high spectrum selectivity and narrow full-width at half-maximum (FWHM) are desired for some specific applications, where detecting a specific wavelength (while suppressing the background emission) is required, like flame detection to explore the existence of a specific kind of chemical element, selected wavelength imaging, fluorescence detection, defense and UV phototherapy [4-5]. PDs convert optical signals into electrical signals through various ways such as photo-emissive, photoconductive and photovoltaic. Due to high sensitivity and fast time of response, ultraviolet (UV) – visible – Infrared (IR) PDs have attracted wide attention [6-7]. Semiconductors materials like CdS, PbS, ZnS, SnS, ZnO, SnO_2, TiO_2, etc. are commonly used in the fabrication of PDs.

Moreover, the development of flexible optoelectronic devices has expanded to a wide range of applications such as fundamental flexible photodetectors, displays, solar cells, optical logic gates, light-emitting diodes (LEDs) and optical-image sensors [8-9]. Utilization of two-dimensional (2D) material is at the forefront of research from the last decade. Due to its strong quantum confinement, tunable electronic properties and a large surface area proved to be their best advantageous properties over other nanostructures. Few more properties in 2D materials like high electron mobility, longer spin lifetime, and excellent mechanical and electrochemical properties make these materials suitable for a wide variety of applications such as photonics, spintronics, energy storage, photocatalytic, thermoelectricity, biomedical applications [10-11]. Moreover, the rapid development of information technology, the optoelectronic devices based on 2D materials have become an indispensable part of the current technological fields [12-17].

Among all semiconductor materials, metal oxides plays very important role in chemistry, physics and materials science. As the metal elements can form a large diversity of oxide compounds and can acquire various structural geometries (1D / 2D / 3D). Metal oxide can show unique electronic properties depending on its shape, size and doping

concentration. In technological applications, metal oxide thin films with thickness ranging from several nanometers up to several micrometers are utilized in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, catalysts, etc.

Synthesis of 2D (thin film) metal oxide nanostructure material can be possible via different techniques and can be put into three distinct groups: Wet Chemical, Physical Vapour Deposition (PVD) and Chemical Vapour Deposition (CVD). Each methodology has associated pros and cons, and careful consideration of the resulting film properties such as crystallinity, microstructure and adhesion must be taken into account before its viable use in device technology.

2. Review of Literature and Development in the Subject:

Solution processed metal oxide thin films are potentially of low cost and are suitable for optoelectronic devices, resistive switching memory devices, sensors, etc. Varity of soluble precursors were thus been explored for this purpose, but their functional performances generally fall short of expectation in terms of low mobility, low current density, process-dependent performance variations, and reliability issues. On the other hand, organometallic compounds has also been utilized for synthesis of metal oxide thin films, but their inherent toxicity and extreme sensitivities to ambient oxygen and moisture over shadow their performance.

Recent literature survey show large number of research reports in the field of metal oxide thin film for application including solar cells, thin film transistors, sensors, resistive switching devices, ferroelectric memories, etc. These films are prepared extensively by physical vapour deposition techniques like Pulsed laser deposition, Atomic layer deposition, Chemical vapour deposition, Sputtering, etc. Whereas, the use of sol gel assisted spin coating and spray pyrolysis techniques are just limited to synthesis of 2D materials required for solar cells, sensors, catalysis, photodetector, etc. as;

Li, Zhenhui et al [18] reported state-of-the-art achievements on typical low-dimensional nanostructured PDs and hybrid PDs. In the 2D nanostructured PDs transition metal dichalcogenides have a natural gap, which promise high sensitivity of photodetection. Graphene and black phosphorus can also stand for 2D nanostructured PDs due to their broadband absorption and tunable direct bandgap, respectively. Nanostructured materials with a number of fascinating and excellent photoelectric properties have promised themselves as versatile building blocks in terms of interconnects and functional units for novel PDs .

Liu, Shuangjie, et al [**19**] summarized the research progress of PDs based on 2D materials some of the technical challenges in wearable and implantable device and possible solutions. The state of art, non-invasive devices show great promising for real-time pathological monitor, health management and tracking. PDs based on flexible substrates have been proved to be feasible in wearable devices (such as UV-radiation monitor, pulse oximeter, etc.) and implantable PDs (such as retinal prosthesis, etc.).

Mu, Congpu, et al [20] reviewed the progress made toward hybrid photodetector based on TMDCs with various sensitizers from metal to large band-gap semiconductor in architectures from zero dimensional quantum dot to two-dimensional crystal .TMDCs have demonstrated great potential for high performance photodetectors due to their large absorption coefficient and high carrier mobility .Hybrid photodetectors based on TMDCs with various sensitizers could offer an effective and low-cost route toward not only the increase of absorption efficiency but also extension of the response range to the infrared regime.

Qiao, Hui, et.al [21} presented a comprehensive summary of the latest research progress of 2D material-based self-powered photodetectors .In addition, we also discussed in depth the self driving mechanism of three self-powered photodetectors and the effect of 2D material structure on device performance .Therefore, 2D material-based self-powered photodetectors have been extensively studied for their excellent optical response performance and have become an important part of self-powered photodetector.

Molina-Mendoza, Aday J., et.a/ [22] reported highly responsive UV-photodetectors based on single electrospun TiO_2 nanofibers. In this work the optoelectronic properties of individual TiO2 fibers produced through coupled sol-gel and electro-spinning with Ti/Au electrodes on SiO_2/Si substrates. The photo response of single electro spun TiO_2 nanofiber-based photodetectors in a wide range of the electromagnetic spectrum (from 375 nm to 1050 nm), finding a good performance in the UV responsivity values up to 90 A·W-1 with an applied voltage of 10 V with 375 nm wavelength and a power density of 15 $W \cdot m^{-2}$. The photodetectors show a time response to the incident light of ~ 5 s, as well as polarization sensitivity with an anisotropy ratio of 12%. Dark current measurements show TiO_2 nanofibers to have a very high conductivity.

Hao, Lanzhong, et. al [23] reported growth of 2D layered SnSe films for UV-Visible-NIR photodetector arrays with high responsitivity. In this study, wafe size SnSe ultrathin films with high uniformity and crystallization are deposited via a scalable magnetron sputtering method .The fabricated SnSe photodetectors demonstrated a UVVisible-NIR

photoresponse, showing an ultrahigh responsivity of 277.3 A W^{-1} with the corresponding external quantum efficiency of 8.5×10^4 % and detectivity of 7.6×10^{11} Jones as well as fast response/recovery speeds.These appreciable performances make 2D SnSe films promising materials in developing high-performance optoelectronic devices.

3. Objectives of Research/proposed Hypothesis

This work investigates the photoconducting properties of metal oxide thin films synthesized using spin coating / spray pyrolysis technique and possible development of highly sensitive and fast responsive optoelectronic device using the deposited film. To achieve the above mention objective this work is made of specific aims;

a. To synthesize metal oxide (MO_x) thin film (pure or doped) on glass/polymer substrate using spray pyrolysis technique.
b. To characterize synthesized thin films using XRD, UV–Vis spectroscopy, Raman spectroscopy, TGA-DTA, SEM-EDS, XPS, etc.
c. To study the photo–conducting properties of MO_x thin film samples using dedicated optoelectronic characterization setup. This includes responsivity, detectivity, response (rise/decay) time, sensitivity, gain, etc.
d. To probe the electronic structure of the film using X-ray photoelectron spectroscopy and understanding the role of its intrinsic properties on charge transport
e. To propose effective photo–detector device based on the results and material properties.

4. Methodology to be adopted

This work includes synthesis of 2D MO_x materials (pure or doped) for its viable application in development of optoelectronic device application. This work designed to run on three stages;

Stage-1: Fabrication of thin films of metal oxide:

The motivation behind this stage is to investigate the growth and physical properties of amorphous and polycrystalline metal oxide films grown on glass / polymer substrate. Individual goals of this stage are

a. Synthesis of high quality 2D MO_x material (pure or doped) on glass / polymer substrate via spin coating or spray pyrolysis technique.

b. Structural, morphological, optical and compositional characterization of the 2D material using XRD, TGA, UV-Vis spectroscopy, Photoluminescence spectroscopy, SEM and AFM.
c. Initial investigation of photoconducting properties of 2D MO_x material with respect to their thickness, dopant concentration, electrode gap.

Stage 2: Establish the electronic structure of the films and correlate with its photoconducting property:

a. Investigation of the electronic structure of the 2D MO_x material (pure or doped) using X-ray photoelectron spectroscopy.
b. Correlating the role of deposition parameters, dopant concentration and film thickness with the observed photoconducting properties.

Stage 3: Development of optoelectronic device based on the obtained results:

The dopants used in this work must be optically active element. Even if it is doped at atomic levels, it induced defect levels must enhance photoconducting property of the film.

a. Investigation of photoconducting properties of 2D MO_x material at various concentrations of Ag/Au/Mn/Co.
b. Use of the above investigated properties of the dopant for determination of viable optoelectronic material based on 2D MO_x material.

During the final stage of the work, efforts will be made to fabricate and demonstrate 2D MO_x material based optoelectronic device for its viable application in current semiconductor market.

5. Importance of study/ Society application:

National status:

A number of important research outcomes addressing a variety of issues in this field are supported and many are in progress in various National laboratories and universities in the country funded by Government of India. Although it is difficult to summarize the whole

effort, a representative cross section of ideas and strategies can be provided as follows: Dr. S. B. Ogale, Dr. Keshav Rajpure, Dr. S. S. Islam, Dr. Rajendra Singh, Dr. S. H. Husale, etc.

International status:

Continuous advancement in device technologies over the past decades has given us devices with powerful capabilities due to advance materials. Many researcher across the globe are working to enhance the performance of PDs [24]. Pei et.al has proposed that CdS nanowires network fabricated on mixed cellulose esters membrane show enhanced photosensitivity due to the polymer molecules which occupy the surface Vs sites leading to the fast photoresponse of this device [25], Shin et.al reports excellent property of nitrocellulose (NC) as a passivation layers or barrier against adsorption of ambient gases on amorphous indium gallium zinc oxide thin film transistors [26] and Lao et.al has shown UV induced in-crease in photoconductance by five orders of magnitude via coating ZnO nanobelt using a polymer (which have a large absorption peak in UV) and owing to an electron-hole generation process as assisted by the energy states in the polymer [27]. Above are few reports that suggest an enhancement in the device functionality is possible via modulating the structure of the device.

In the specific research area to be focused upon in this work, the international research is just beginning to grow creating an open opportunities for Indian science to take a lead and make a substantial impact. These developments are occurring in the domains of new device concepts. Few impressive examples who flourish the focus of this project are: Dr. S. Sawyer, Dr. U. Jeong, Dr. Z. L. Wang, Dr. Y. A. Zhang, Dr. H. J. Kim, etc. Lots of literature is available on various reputed research journals like: Nature, Science, Advanced Materials, Nano Letters, Advanced Functional Materials, etc.

Significance of the study

In recent years, extensive research is going on in the area of synthesis of highly functional 2D MO_x material owing to its promising applications in the field of opto or nano-electronic devices. Recent reports has shown 2D MO_x material based light-emitting diodes, photo-detectors, solar cells, thin film transistors, etc. These thin films have been prepared by various physical and chemical methods, including vacuum evaporation, sputtering, electro deposition, molecular beam epitaxy, photochemical deposition, spray pyrolysis, metal organic chemical vapour deposition, chemical bath deposition, screen printing and sol-gel assisted spin coating method. All these techniques do have several merits and

limitations. Among these techniques, the spin coating or spray pyrolysis method gives higher coating area, high superior homogeneity, high purity, better micro structural control and narrow thickness variation as compared with those prepared by physical methods. The spin coating or spray pyrolysis method have additional advantages like its simplicity, cost effectiveness and its ability to deposit uniform films, moreover, its reproducibility in a relatively shorter processing time at lower temperatures is remarkable. Current electronic industries need a method, which is low-cost, and large-scale integration.

This work focuses on the connectivity between the pure and doped platforms based on photoconductivity in 2D MO_x material; emphasizing synergetic integration with potential for novel effects exclusive to the hybrid concept.

It is worth to mention here that the dilute doping of metal/impurity atoms in oxide matrix significantly modify its physical properties like luminescence, transport, etc. by modulating the defect (oxygen vacancies) concentration around it, to maintain the charge balance in the material. This was investigated in past few years, where a 2D MO_x material matrix doped with optically active metal atom behaves like highly luminescent semiconductor.

6. Proposed work Plan/ Formulation and Structure of Study: Year-wise Plan of work and targets to be achieved

First year:

a. Initiate synthesis of pure 2D MO_x material (TiO_2, ZnO , SnO_2)
b. Initiate and optimize thin film growth methods (spin coating / spray pyrolysis) for synthesis of functional 2D MO_x material.
c. Study the effect of temperature and substrate on film morphology.
d. Perform extensive characterization including UV-Vis, XRD, AFM, TGA, SEM-EDS and XPS to study the structural, morphological, optical and electronic properties of synthesized thin film.
e. Initiate testing of photoconducting properties of pure 2D MO_x material.

Second year:

a. Initiate and optimize deposition technique for doping of functional 2D MO_x material with optically active elements.
b. Initiate and optimize thin film growth methods (spin coating / spray pyrolysis) for doped functional 2D MO_x materials.

c. Study effect of temperature, doping concentration and substrate on film morphology.
d. Perform extensive characterizations including UV-Vis, XRD, AFM, TGA, SEM–EDS and XPS to know the structural, morphological, optical and electronic properties of doped 2D MO_x materials.
e. Test of device properties of doped 2D MO_x materials.
f. Start publishing research papers .

Third year:

a. Review the status of progress during the first two years and take appropriate steps towards the most effective utilization of the knowledge , facilities and experience during the remaining duration .
b. Continue to analyze the data obtained and proceed with publications / petenting as appropriate.
c. Prepare thesis for submission.

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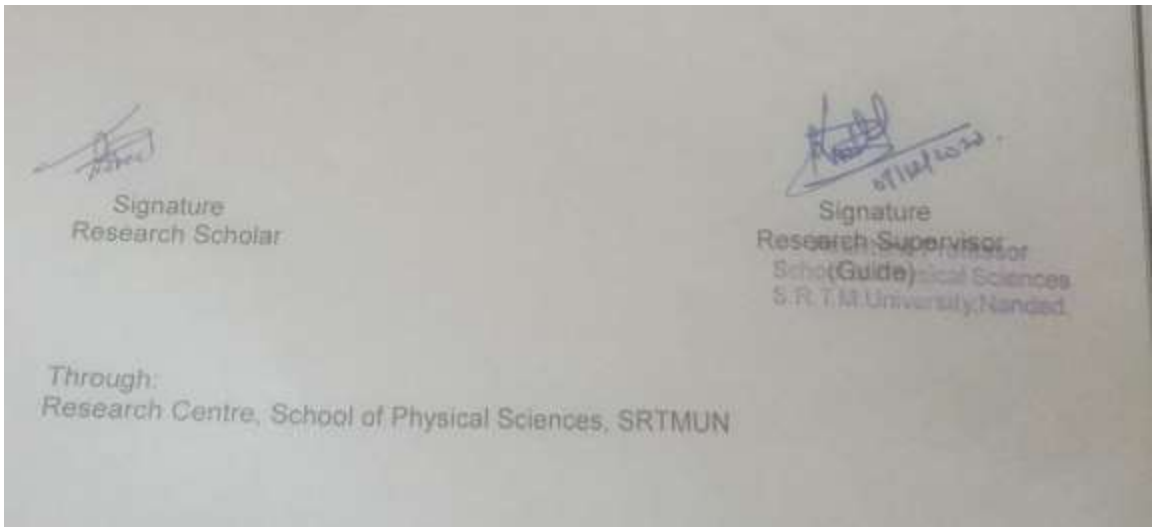
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